

Organic Bulk Heterojunction Solar Cells Based on Poly(*p*-Phenylene-Vinylene) Derivatives

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1. Introduction

Since the discovery of electrical conductivity in chemically doped polyacetylene (Shirakawa et al., 1977; Chiang et al., 1977; Chiang et al., 1978), enormous progress has been made in the design, synthesis and detailed studies of the properties and applications of π -conjugated polymers (Yu et al., 1998; Skotheim et al., 1998; Hadziioannou et al., 1998). The award of the Nobel prize in Chemistry three decades later in the year 2000 to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for the abovementioned discovery and development of semiconducting polymers, was greeted worldwide among researchers as a recognition for the intensified research, which has been going on in the field of organic π -conjugated polymers (Shirakawa, 2001). Such polymers are advantageous compared to inorganic semiconductors due to their low production cost, ease of processability, flexibility as well as tenability of their optical and electronic properties through chemical modifications. These outstanding properties make them attractive candidates as advanced materials in the field of photonics and electronics (Forrest, 2004; Klauk, 2006; Bao & Locklin, 2007; Sun & Dalton, 2008; Moliton, 2006; Hadziioannou & Mallarias, 2007; Shinar & Shinar, 2009; Nalwa, 2008).

Among the most used polymers in optoelectronic devices are the poly(*p*-phenylene-vinylene)s (PPV), polyfluorenes, polythiophenes and their derivatives. The insertion of side-chains in these polymers reduces the rigidity of the backbone, increases their solubility and enables the preparation of films through inexpensive, solution-based methods, such as spin-coating (Akcelrud, 2003). Besides, these ramifications can also be used to tune the photophysical and electrochemical properties of these polymers using a variety of routes.

Solar cells based on solution-processable organic semiconductors have shown a considerable performance increase in recent years, and a lot of progress has been made in the understanding of the elementary processes of photogeneration (Hoppe & Sariciftci, 2004; Mozer & Sariciftci, 2006; Günes et al., 2007). Recently, organic bulk heterojunction solar cells with almost 100% internal quantum yield were presented, resulting in up to almost 8% power conversion efficiency (Park et al., 2009; Green et al., 2010). This device concept has

been shown to be compatible with solution-processing at room temperature, for instance, by high-throughput printing techniques. Processing on flexible substrates is possible, thus allowing for roll-to-roll manufacturing as well as influencing the properties of the finished electronic devices. The recent considerable achievements in terms of power conversion efficiency have been made possible now by more than 15 year long research and development on solution-processed organic solar cells. Nevertheless, in order to let the scientific progress be followed by a commercial success, further improvements in term of efficiency and device lifetime have to be made.

In this chapter, we will briefly introduce the basic working principles of organic solar cells and present an overview of the most often studied PPV-type materials as applied within the photoactive layer.

2. Organic solar cells

2.1 A brief history

The first organic solar cells consisted of a single layer of photoactive material sandwiched between two electrodes of different work functions (Chamberlain, 1983; Wohrle & Meissner, 1991). However, due to the high binding energy of the primary photoexcitations, the separation of the photogenerated charge carriers was so inefficient that far below 1% power conversion efficiency could be achieved.

The next breakthrough was achieved in 1986 by introducing the bilayer heterojunction concept, in which two organic layers with specific electron or hole transporting properties were sandwiched between the electrodes (Tang, 1986). In this organic bilayer solar cell were consisting of a light-absorbing copper phthalocyanine layer in conjunction with an electronegative perylene carboxylic derivative. The differing electron affinities between these two materials created an energy offset at their interface, thereby driving exciton dissociation.

The efficiencies of the first organic solar cells reported in the 1980s were about 1% at best at that time. Primarily, this is due to the fact that absorption of light in organic materials almost always results in the production of a mobile excited state, rather than free electron-hole pairs as produced in inorganic solar cells. This occurs because in organic materials the weak intermolecular forces localize the exciton on the molecules. Since the exciton diffusion lengths in organic materials are usually around 5-15 nm (Haugeneder et al., 1999), much shorter than the device thicknesses, exciton diffusion limits charge-carrier generation in these devices because most of them are lost through recombination. Photogeneration is therefore a function of the available mechanisms for excitons dissociation.

The discovery of ultrafast photoinduced electron transfer (Sariciftci et al., 1992) from a conjugated polymer to buckminsterfullerene (C_{60}) and the consequent enhancement in charge photogeneration provided a molecular approach to achieving higher performances from solution-processed systems. In 1995 the first organic bulk heterojunction organic solar cell was fabricated based on a mixture of soluble *p*-phenylene-vinylene (PPV) derivative with a fullerene acceptor (Yu et al., 1995). In 2001, Shaheen et al. obtained the first truly promising results for bulk heterojunction organic solar cells when mixing the conjugated polymer poly(2-methoxy-5-(3',7'-dimethyl-octyloxy)-*p*-phenylene vinylene) (MDMO-PPV) and methanofullerene [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM) yielding a power conversion efficiency of 2.5% (Shaheen et al., 2001).

Padinger *et al.* (Padinger *et al.*, 2003) presented a further increase in the power conversion efficiency by using a blend, which is nowadays the best investigated organic solar cell system: a poly(3-hexyl thiophene) donor (P3HT) in conjunction with PCBM. It was shown that annealing at a temperature above the glass transition of the polymer enabled an enhancement of the efficiency from 0.4% to 3.5%.

In the following years, the power conversion efficiency could be increased steadily. This is, to a large fraction, due to the considerable amount of time that has been spent by many laboratories around the world on the optimization of bulk heterojunction solar cells—many of them using P3HT:PCBM—but also by new approaches. Additives have been used in order to allow an increased control of the phase segregation during film formation of a copolymer–fullerene blend (Park *et al.*, 2009; Peet *et al.*, 2007), thus yielding efficiencies of up to 6%. The process additive is a solvent for the fullerene, but not the polymer, thus allowing the PCBM an extended time for self-organization during the drying process. A positive effect by heating the solvent before the film application could also be shown (Bertho *et al.*, 2009). Today, up to 8% power conversion efficiency are reported in this kind of organic solar cells (Park *et al.*, 2009; Green *et al.*, 2010).

2.2 Organic bulk heterojunction solar cells

The sequential process involved in the light into electricity conversion can be summarized by the following steps: First, incident light is absorbed within the photoactive layer leading to the created of a bound electron-hole pairs (singlet excitons); the created excitons start to diffuse within the donor phase leading to charge separation; the separated charge carriers are transported to the corresponding electrodes.

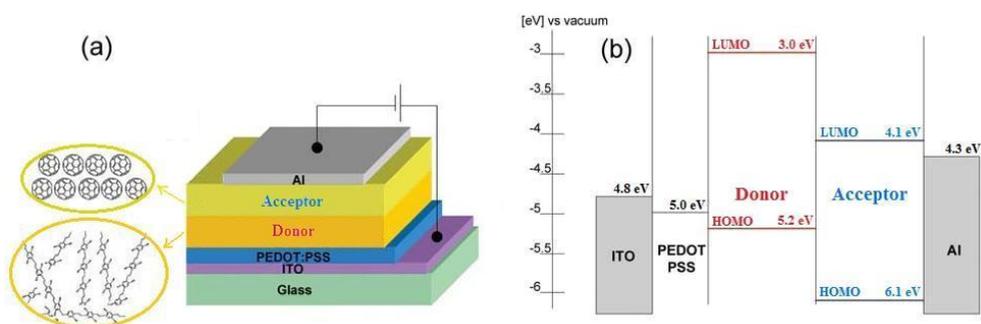


Fig. 1. (a) Schematic device structure and (b) energy diagram for an organic bilayer solar cell

Figure 1 (a) shows the simplest structure of an organic bilayer solar cell appears to be the superposition of donor and acceptor materials on top of each other, providing the interface needed to ensure the charge transfer. The schematic energy diagram of such an organic bilayer solar cell is depicted in Figure 1 (b). The excitons photogenerated in the donor or in the acceptor can diffuse to the interface where they are dissociated. According to the Onsager theory (Onsager, 1938) that can be invoked as a first approximation in organic semiconductors, photoexcited electrons and holes, by virtue of the low dielectric constant intrinsic to conjugated polymers, are coulombically bound. Due to the related exciton binding energy, which with around 0.5 eV is much larger than the thermal energy, the photogenerated excitons are not easily separated. Once excitons have been generated by the

absorption photons, they can diffuse over a length of approximately 5-15 nm (Haugeneder et al., 1999). Since the exciton diffusion lengths in conjugated polymers are less than the photon absorption length, the efficiency of a bilayer cell is limited by the number of photons that can be absorbed within the effective exciton diffusion range at the polymer/electron interface. This limits drastically the photocurrent and hence the overall efficiency of the organic bilayer solar cells. To overcome this limitation, the surface area of the donor/acceptor interface needs to be increased. This can be achieved by creating a mixture of donor and acceptor materials with a nanoscale phase separation resulting in a three-dimensional interpenetrating network: the “bulk heterojunction solar cells” (Figure 2).

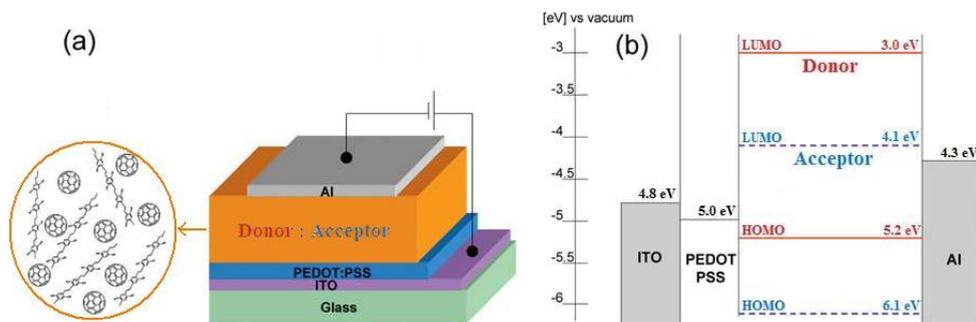


Fig. 2. (a) Schematic device structure and (b) energy diagram for an organic bulk heterojunction solar cell

The discovery of 1-(3-methoxycarbonyl)propyl-1-phenyl[6]C₆₁ (PCBM) (Hummelen et al., 1995), a soluble and processable derivative of fullerene C₆₀, allowed the realization of the first organic bulk heterojunction solar cell by blending it with poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV) (Yu et. Al., 1995). Figure 2(b) demonstrates the schematic energy diagram of an organic bulk heterojunction solar cell. Contrary to Figure 1(b), excitons experience dissociation wherever they are generated within the bulk. Indeed, the next interface between donor and acceptor phases is present within the exciton diffusion length everywhere in the device. After having been generated throughout the bulk, the free carriers have to diffuse and/or be driven to the respective electrodes (Dennler & Sariciftci, 2005).

2.3 Characteristics of bulk heterojunction solar cells

Conjugated polymer thin films sandwiched between two metal electrode are usually described using a metal-insulator-metal (MIM) picture (Parker, 1994). The different operating regimes the MIM device due to externally applied voltages is shown in Figure 3. As illustrated in Figure 3(a), the vacuum levels (E_{vac}) of the stacked materials shall align themselves (Schottky-Mott model).

Figure 3(a) indicates the energy diagram of a bulk heterojunction solar cell in open circuit condition. The E_{vac} of the different materials are aligned as explained above, and no electrical field is present within the device. Figure 3 (b) represents the short circuit condition. The Fermi levels of the two electrodes align themselves and a built-in field appears in the bulk, resulting in a constant slope for the HOMO and LUMO levels of the donor and acceptor (respectively, HD, LD, HA, and LA) and for the E_{vac} .

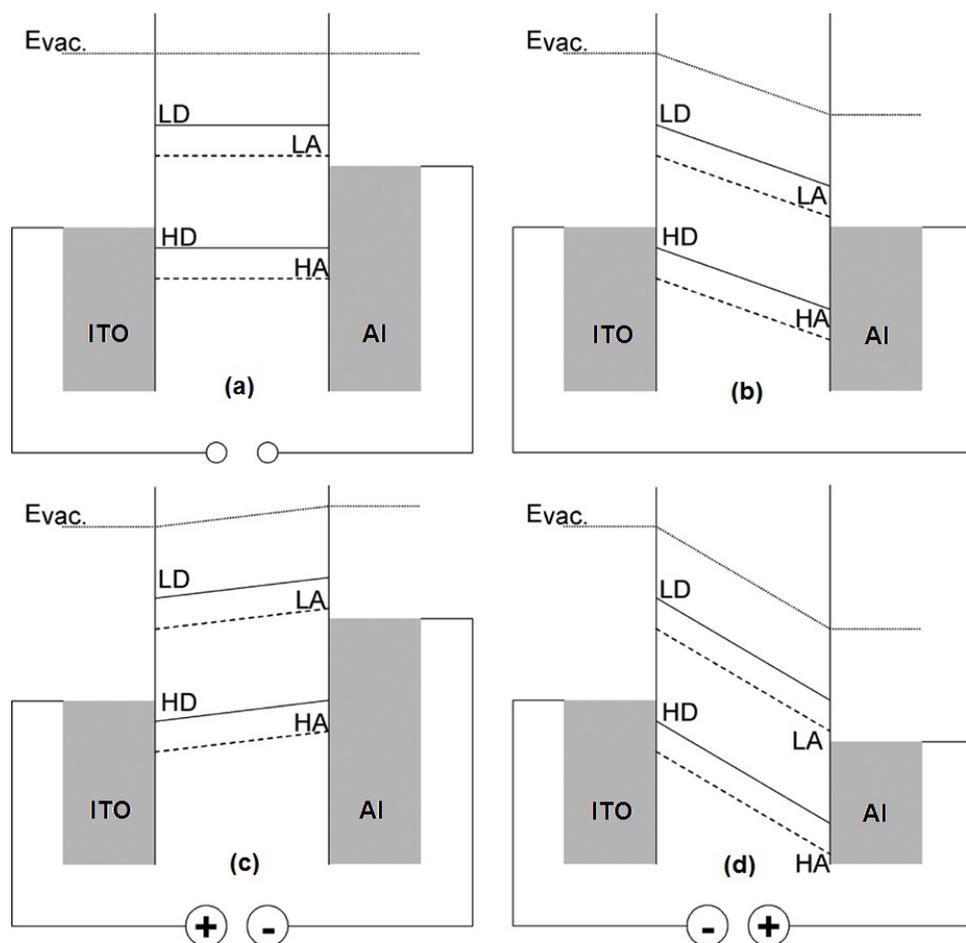


Fig. 3. MIM picture for a polymer diode under different operating modes. (a) open circuit condition, (b) short circuit condition, (c) forward bias, (d) reverse bias.

When polarized in the forward direction (high work function electrode (ITO) connected to (+) and low work function electrode (Al) connected to (-)) as in Figure 3 (c), electrons can be injected from the Al electrode to ITO electrode and holes from ITO electrode to Al electrode. The effective field in the device will ensure the drift of electrons from Al electrode to ITO electrode and hole from ITO electrode to Al electrode. Finally, when the device is polarized in the reverse direction (ITO connected to (-) and Al connected to (+)) (Figure 3 (d)), charge injection is hindered by the field present in the device (Dennler & Sariciftci, 2005).

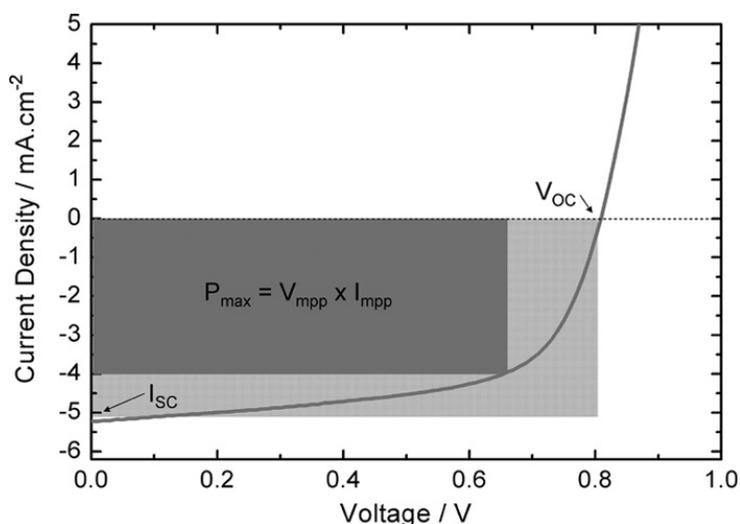


Fig. 4. First and fourth quadrant of a typical J - V curve observed for a Glass/ITO/PEDOT:PSS/MDMO-PPV:PCBM(1:4)/Al solar cell. Shown are the short circuit current (I_{sc}), the open circuit voltage (V_{oc}), the current (I_{mpp}) and voltage (V_{mpp}) at the maximum power point (P_{max})

Solar cells are operated between open circuit and short circuit condition (fourth quadrant in the current-voltage characteristics), as shown in Figure 4. In the dark, there is almost no current flowing, until the contacts start to inject heavily at forward bias for voltages larger than the open circuit voltage. Under illumination, the current flows in the opposite direction than the injected currents. The overall efficiency of a solar cell can be expressed by the following formula:

$$\eta = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} \quad (1)$$

where V_{oc} is the open circuit voltage, I_{sc} is the short circuit current, and P_{in} is the incident light power. The fill factor (FF) is given by

$$FF = \frac{I_{mpp} \cdot V_{mpp}}{V_{oc} \cdot I_{sc}} \quad (2)$$

where I_{mpp} and V_{mpp} represent the current and voltage at the maximum power point (P_{max}) in the fourth quadrant, respectively (Figure 4).

3. p -phenylene-vinylene based conjugated polymers

3.1 Poly(p -phenylene-vinylene) and its derivatives

Poly(p -phenylene-vinylene)s (PPVs) and its derivatives are one of the most promising classes of conjugated polymers for organic solar cells due to their ease of processability as

well as tunability of their optical and electronic properties through chemical modifications. Since the first report of electroluminescence from PPV, a great research attention has been focused on these types conjugated polymers (Burroughes et al., 1990). This focus was moreover up heaved after the discovery of an ultrafast photoinduced charge transfer from alkoxy-substituted PPV to the buckminsterfullerene (Sariciftci et al., 1992). PPV and its derivatives remain the most popular conjugated polymers for this application and continue to generate considerable interest and much research for photovoltaic applications (Cheng et al., 2009).

The pure PPV is insoluble, intractable, and infusible and therefore difficult to process. Solution processability is desirable as it allows polymeric materials to be solution cast as thin films for various applications. A general methodology to overcome this problem is to develop a synthetic route that involves a solution-processable polymer precursor. First synthetic route for high quality PPV films with high molecular weights was first introduced by Wessling (Figure 5) allowed the synthesis of soluble precursors, which can be processed into thin films prior to thermal conversion to PPV (Wessling & Zimmerman, 1968; Wessling, 1985). A potential drawback of the precursor routes is the limited control over polydispersity and molecular weight of the resulting polymer.

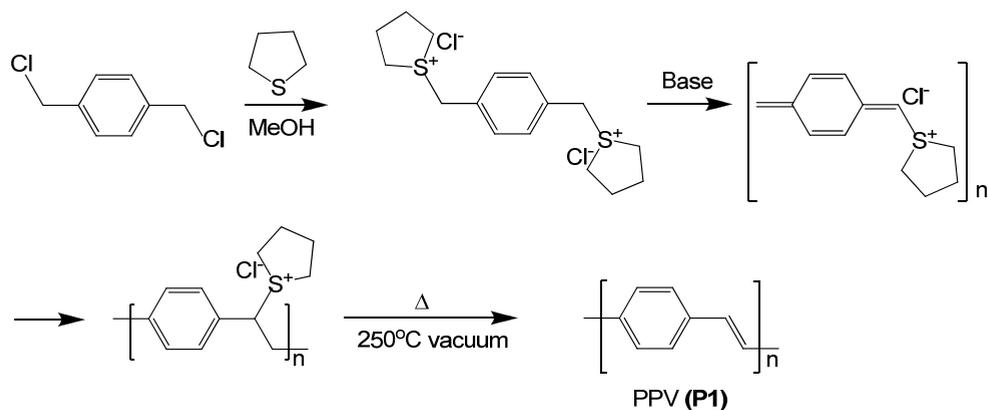


Fig. 5. Synthesis of PPV (**P1**) via the Wessling Route

Some of the drawbacks of this precursor approach include the generation of toxic side products during the solid state elimination process, structural defects arising from incomplete thermal conversion or oxidation, and undefined molecular weights and distribution (Papadimitrakopoulos et al., 1994). By incorporating long alkyl or alkoxy chains into the phenylene ring before polymerization to ensure the solubility, a one step approach can be applied to make processable PPV derivatives which can then be cast into thin films directly without conversion for device fabrication (Braun & Heeger, 1991). To date, the most widely used method for the preparation of PPV derivatives is the Gilch route (Gilch, 1966). A typical Gilch route to the synthesis of a representative solution-processable poly(2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylene-vinylene) (MEH-PPV, **P2**) is represented in Figure 6 (Neef & Ferraris, 2000). By following the same synthetic route, poly(2-methoxy-5-((3',7'-dimethyloctyl)oxy)-1,4-phenylenevinylene) (MDMO-PPV, **P3**) can also be synthesized

(Figure 7). This route involves mild polymerization conditions, and the molecular weights of the polymers obtained are generally high (Cheng et al., 2009).

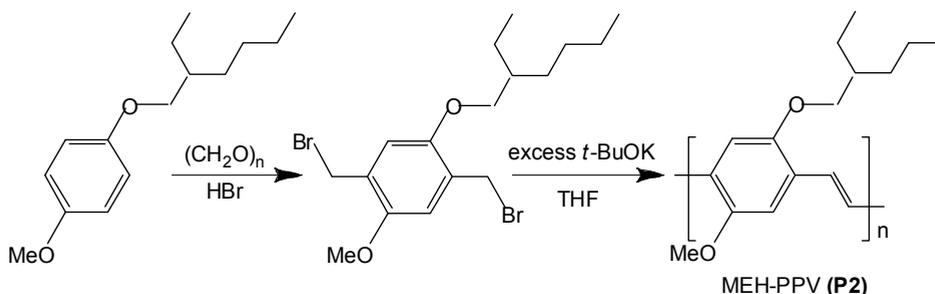


Fig. 6. Synthesis of MEH-PPV (**P2**) via the Gilch Route

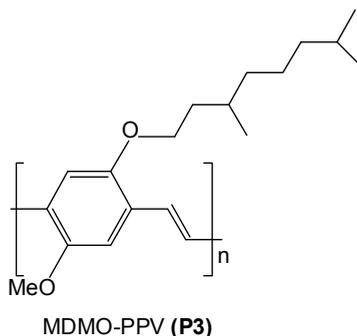


Fig. 7. Chemical structure of MDMO-PPV (**P3**)

Solution-processable PPV derivatives were first reported by Wudl et al. (Wudl et al., 1991; Braun & Heeger, 1991) and by Ohnishi et al. (Doi et al., 1993). The solubility of the materials was achieved by grafting of long alkoxy chains, which cause some conformational mobility of the polymers. Consequently the soluble derivatives have lower glass transition temperatures than pure PPV. Poly[(2,5-dialkoxy-1,4-phenylene)-vinylene]s including long alkoxy side chains are soluble in common organic solvents such as chloroform, toluene, chlorobenzene, dichloromethane, tetrahydrofuran. Fig. 8 shows the chemical structures of PPV and its various alkoxy-substituted derivatives. The solubility increases from left to right, whereby the solubility of the much studied MEH-PPV and MDMO-PPV is enhanced by the branched nature of their side chains (Braun & Heeger, 1991).

PPV derivatives are predominantly hole conducting materials with high-lying LUMO (lowest unoccupied molecular orbital) levels. The unbalanced charge carrier transport properties and the relatively high barrier for electron injection from electrode metals such as aluminium limit the efficiency of the photovoltaic devices.

Several approaches have been explored to improve the electron affinity of PPVs. The insertion of weak electron-withdrawing triple bonds ($-C\equiv C-$) within the PPV backbone can be regarded as one of the most original approach of enhancing the electron affinity of PPVs (Brizius et al., 2000; Egbe et al., 2001).

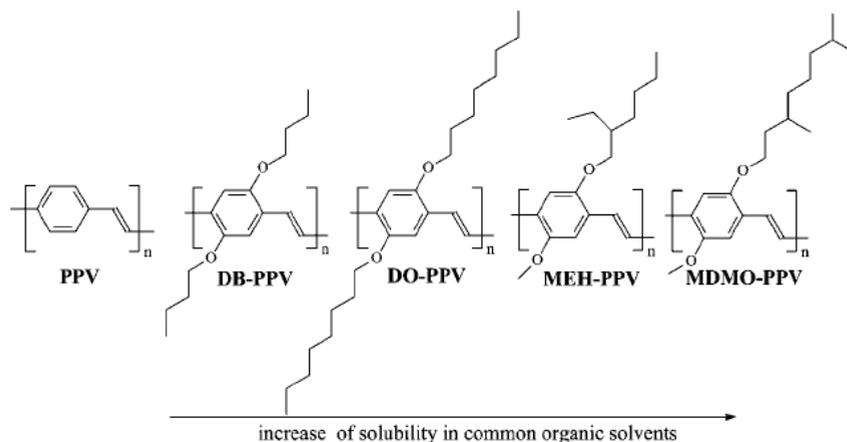


Fig. 8. Chemical structures of PPV and its different alkoxy-substituted derivatives

The substituent on the phenylene ring of PPV allows for the tuning of the band gap. Enhanced electron affinity of substituted PPVs is reflected by higher absorption coefficients, lower-lying HOMO (highest occupied molecular orbital) levels, and higher open circuit voltages from fabricated organic solar cells. The HOMO and LUMO levels of unsubstituted PPV are reported to be ca. -5.1 and -2.7 eV, respectively, with a band gap around 2.4 eV. Introducing two alkoxy groups into the phenylene ring to perturb the molecular orbitals lowers the LUMO to -2.9 eV with an essentially unchanged HOMO level. Hence, the band gap is reduced to 2.2 eV (Alam & Jenekhe, 2002). As a consequence, PPV emits a green-yellow light, while MEH-PPV exhibits a yellow-orange emission. Because PPV derivatives are the earliest conjugated polymers developed for organic electronics application, they were also frequently used as the active materials in organic bilayer solar cells before the concept of bulk heterojunction configuration was widely accepted. For organic bilayer solar cells, PPV and MEH-PPV serve as the electron donor in conjunction with a poly(benzimidazobenzophenanthroline ladder) (BBL, **P4**) as the electron acceptor (Figure 9). The photovoltaic parameters of the bilayer device with the configuration ITO/PPV/**P4**/Al showed a J_{sc} of 2.3 mA/cm², a V_{oc} of 1.06 V, an FF of 47%, and power conversion efficiency (PCE) value of 1.4%. In case of using MEH-PPV as the electron donor, the device reached a PCE of 0.8% under the same conditions (Alam & Jenekhe, 2004). The better photovoltaic performance of PPV over MEH-PPV can be accredited to the greater crystallinity and structural order of the PPV main chain compared to alkylated MEH-PPV.

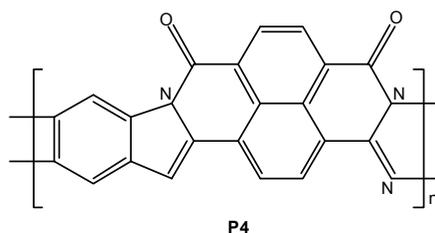


Fig. 9. Chemical structure of BBL **P4**

Soluble MEH-PPV was also combined with PCBM for organic solar cell applications. The organic bilayer solar cell with the configuration ITO/PEDOT:PSS/MEH-PPV/PCBM/Al showed a J_{sc} of 2.1 mA/cm², a V_{oc} of 0.75 V, an FF of 23%, and a PCE value of 0.46% (Zhang et al., 2002). An organic bulk heterojunction solar cell including MEH-PPV/PCBM as the photoactive layer showed better PCE values in the range 1.1-1.3% than bilayer solar cells. Furthermore, by stacking two independent single organic solar cells together with the help of the transparent cathode LiF/Al/Au, the PCE of the multiple-device stacked structure can be dramatically improved to 2.6% (Shrotriya et al., 2006). The devices can be stacked together and connected either in parallel or in series, resulting in doubled J_{sc} or V_{oc} , respectively, compared to those of a single device (Cheng et al., 2009).

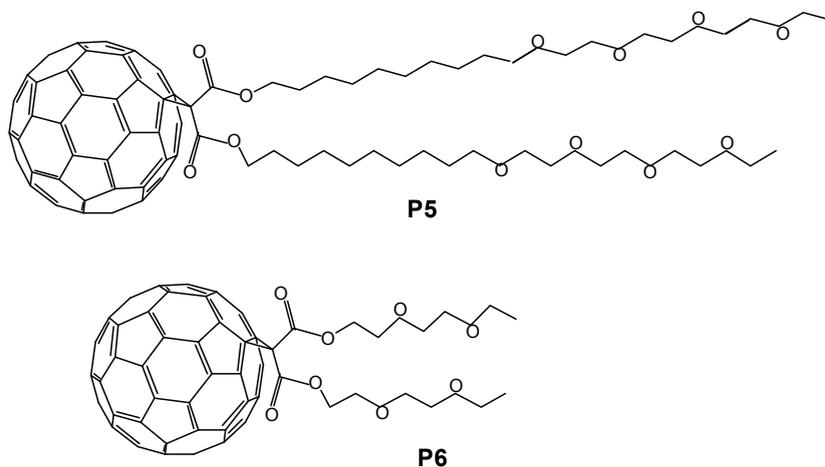


Fig. 10. Chemical structures of C₆₀ derivatives **P5** and **P6**

Two alternative soluble methanofullerene derivatives **P5** and **P6** have been developed to serve as electron acceptors and combined with MEH-PPV to produce organic solar cells. The chemical structures of the C₆₀ derivatives are shown in Figure 10. Due to a better compatibility of **P5** with MEH-PPV, the MEH-PPV/**P5** system shows a better device PCE of 0.49% than the MEH-PPV/**P6** system, which has a PCE of 0.22% (Li et al., 2002). In addition to C₆₀ derivatives, different types of titanium oxide (TiO₂) were blended with MEH-PPV for photovoltaic device applications (Breeze et al., 2001; Song et al., 2005; Wei et al., 2006; Neyshtadt et al., 2008; Shim et al., 2008). However, their device performances were generally low, with PCE values lower than 0.5% (Cheng et al., 2009).

In organic bulk heterojunction solar cells, MDMO-PPV is the most widely used PPV derivative to serve as the electron donor in combination with C₆₀ electron acceptor derivatives. Organic solar cells based on combined MDMO-PPV:PCBM (1:4, w/w) were fabricated by Shaheen and co-workers (Shaheen et al., 2001). It was found that when chlorobenzene was used as the casting solvent instead of toluene to deposit the active layer, an optimal morphology with suppressed phase segregation and enhanced microstructure was obtained, resulting in increased charge carrier mobility for both holes and electrons in the active layer. And this device achieved a J_{sc} of 5.23 mA/cm², a V_{oc} of 0.82 V, and a high PCE of 2.5% (Shaheen et al., 2001).

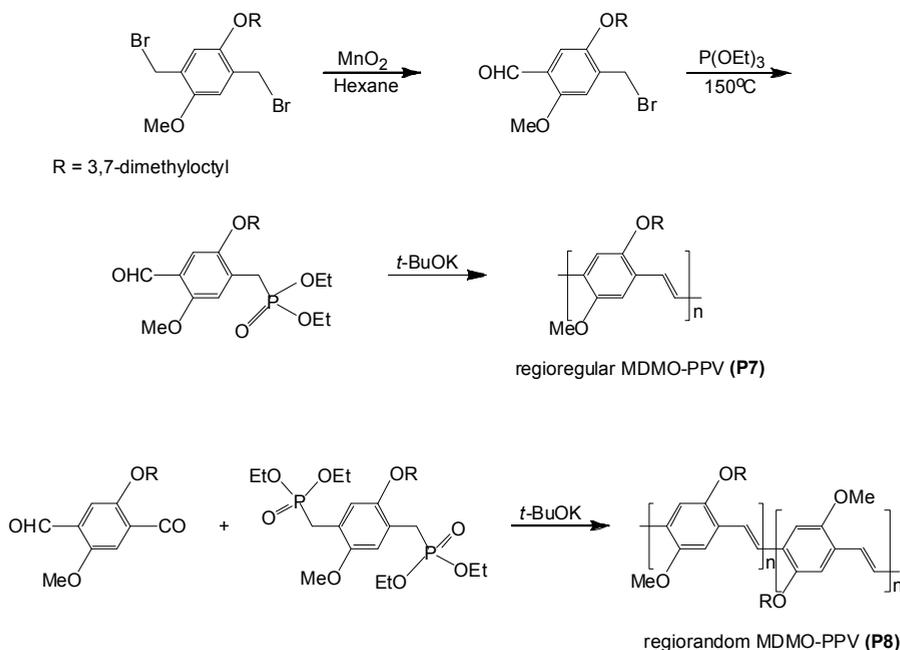


Fig. 11. Synthesis of regioregular and regiorandom MDMO-PPVs (**P7**) and (**P8**)

Regioregularity in MDMO-PPV also plays an important role in determining the photovoltaic device performance. A fully regioregular MDMO-PPV (**P7**) by the Wittig-Hornor reaction of a single monomer comprised of aldehyde and phosphonate functionalities was synthesized (Tajima et al., 2008). Regiorandom MDMO-PPV (**P8**), from dialdehyde and diphosphonate monomers, was also prepared for comparison (Figure 11). The device achieved a PCE of 3.1%, a J_{sc} of 6.2 mA/cm², a V_{oc} of 0.71 V, and an FF of 70% with regioregular MDMO-PPV (**P7**). This is the highest efficiency reported for the PPV:PCBM system so far. But the device based on regiorandom MDMO-PPV (**P8**)/PCBM only achieved a PCE of 1.7%. It is concluded that higher crystallinity of the polymer for higher hole mobility and better mixing morphology between the polymer and PCBM contribute to the improvement of photovoltaic device performance with regioregular MDMO-PPV (Cheng et al., 2009).

Miscellaneous physics and engineering aspects have been investigated for devices based on the MDMO-PPV/PCBM bulk heterojunction active layer system: photooxidation (Pacios et al., 2006), stacked cells (Kawano et al., 2006), active layer thickness (Lenes et al., 2006), NMR morphology studies (Mens et al., 2008), and insertion of a hole-transporting layer between PEDOT and the active layer (Park et al., 2007). Besides the PCBM organic acceptor, inorganic electron acceptors (van Hal et al., 2003; Beek et al., 2005; Boucle et al., 2007; Sun et al., 2003) such as metal oxides or quantum dots are also under active development and have been combined with MDMO-PPV to prepare hybrid (organic-inorganic) bulk heterojunction solar cells. Optimized photovoltaic devices using blends of MDMO-PPV:ZnO (Beek et al., 2005) or MDMO-PPV:cadmium selenide (Sun et al., 2003) showed moderate PCE values of 1.6% and 1.8%, respectively.

3.2 Cyano-substituted poly(*p*-phenylene-vinylene)s

Cyano-substituted poly(*p*-phenylene-vinylene)s (CN-PPV) with electron deficient cyano groups on the vinyl units are synthesized by Knoevenagel polycondensation polymerization of terephthalaldehyde and 1,4-bis(cyanomethyl)benzene in the presence of the base *t*-BuOK (Figure 12). Hence, the LUMO and HOMO levels of PPV derivatives can also be tuned by incorporating electronic substituent into the vinylene bridges (Cheng et al., 2009).

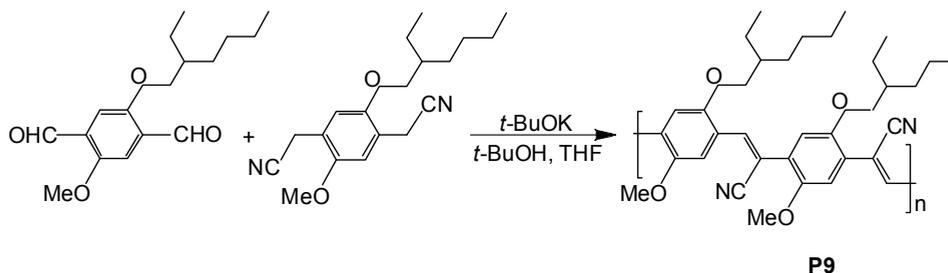


Fig. 12. Synthesis of CN-PPV copolymer **P9** via a Knoevenagel Polycondensation

CN-PPVs show high electron affinity to reduce the barrier to electron injection and good electron-transport properties as a result of the electron-withdrawing effect of the cyano side group and suitable electron acceptors in organic photovoltaic devices (Granström et al., 1998; Halls et al., 1995; Gupta et al., 2007). To effectively reduce the band gap of CN-PPV below 2 eV, electron-rich thiophene units with lower aromaticities have been incorporated into the main chain to form a D-A arrangement. A series of copolymers based on the bis(1-cyano-2-thienylvinylene)phenylene structures with different alkyl or alkoxy side chains on the thiophene rings were reported by Vanderzande et al. (Colladet et al., 2007) (Figure 13).

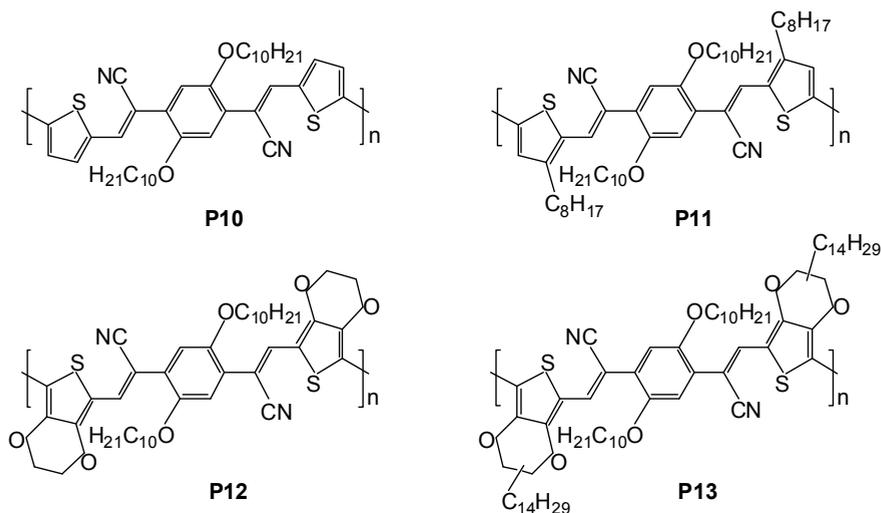


Fig. 13. Chemical structures of **P10-P13**

These monomers were all prepared by Knoevenagel condensations to construct cyanovinylene linkages. The electron-rich nature of thiophene units in these polymers makes them good candidates to serve as electron donors in organic bulk heterojunction solar cells. For example, both **P11**/PCBM- and **P12**/PCBM-based solar cells achieved a PCE of around 0.14%. Optimization of these devices by thermal annealing showed a slight increase of PCE to 0.19%. Reynold et al. also reported synthesizing a range of CN-PPV derivatives (**P14-P17**) containing dioxothiophene moieties in the polymer main chain (Figure 14) (Thompson et al., 2005; Thompson et al., 2006). The best photovoltaic device based on these CN-PPV derivatives with PCBM as the active layer achieved a PCE of 0.4%.

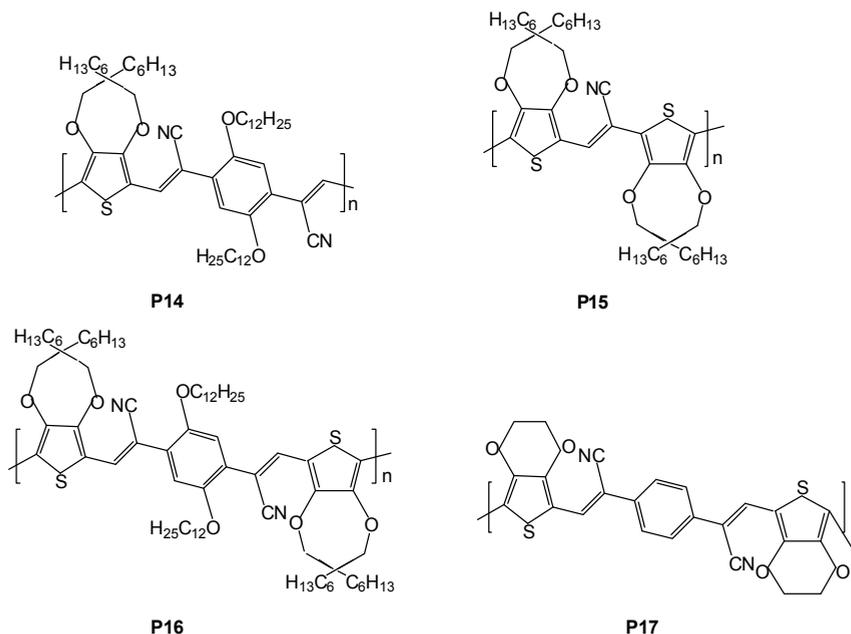
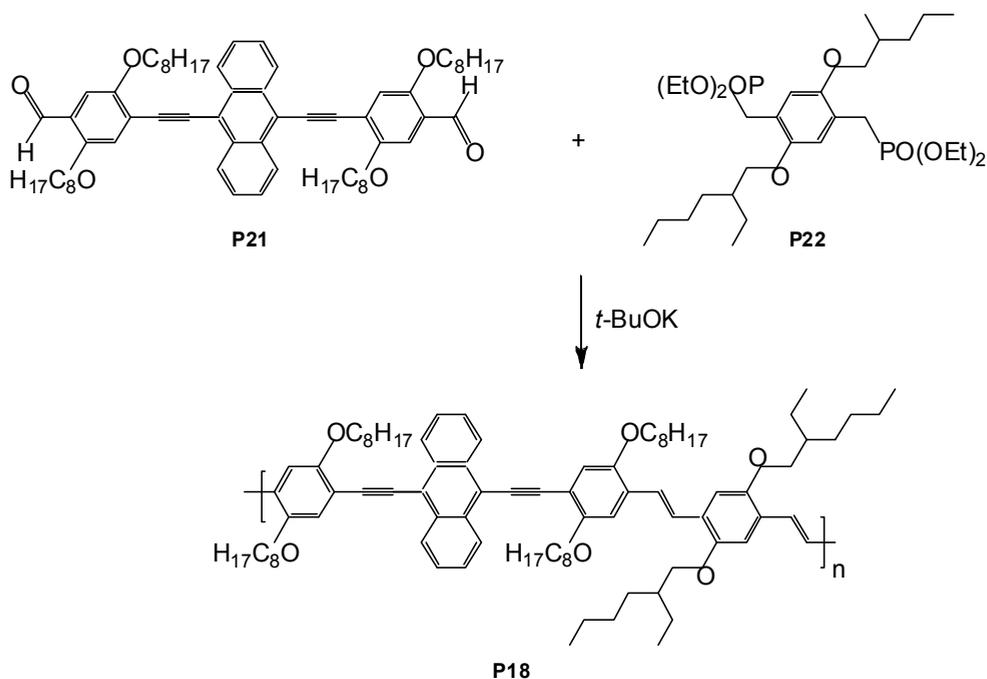
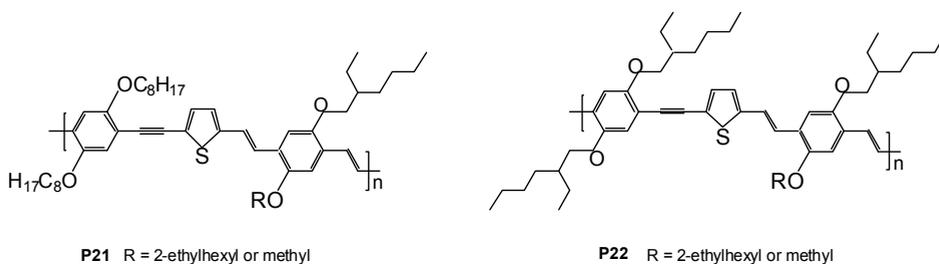
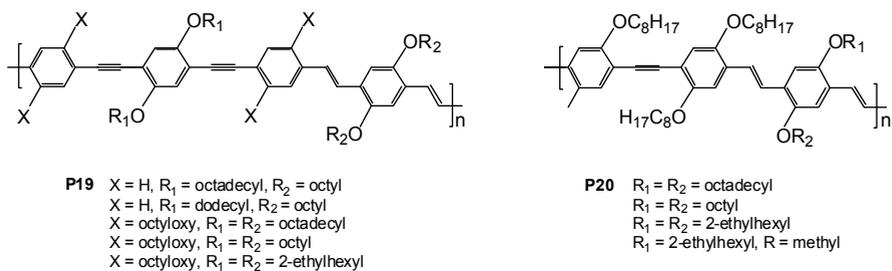


Fig. 14. Chemical structures of **P14-P17**

3.3 Acetylene-substituted poly(*p*-phenylene-vinylene)s

Acetylene-substituted PPV derivatives can be synthesized via the Wittig - Horner Reaction (Figure 15). The coplanar and rigid nature of the acetylene moiety in the polymer chain may have the potential to obtain a higher degree of packing and thus improve the photovoltaic performance of such devices. Having coplanar electron-rich anthracene units and triple bond bridges, **P18** exhibits broader absorption, a lower HOMO level, and a smaller optical band gap of 1.9 eV, compared to MDMO-PPV. A device with the configuration of ITO/PEDOT/**P18**:PCBM (1:2, w/w)/LiF/Al, achieved a PCE value of up to 2% with a high V_{oc} of 0.81 V. Figure 16 shows the chemical structures of a series of acetylene-substituted PPV derivatives synthesized by similar procedures. For polymers **P21** and **P22** (Egbe et al., 2007), the introduction of a thiophene ring into the polymer backbone showed an improvement in the PCE ranging from 1.2% to 1.7%. This is higher than those for **P19** and **P20** (Egbe et al., 2005), based on the same device configuration of ITO/PEDOT/polymer:PCBM (1:3, wt%)/LiF/Al (Cheng et al., 2009).

Fig. 15. Synthesis of acetylene-containing **P18** via a Wittig – Horner reactionFig. 16. Chemical structures of acetylene-containing PPV derivatives **P19-P22**

4. Conclusion

The efficiency of organic solar cells is increasing steadily by means of interdisciplinary approach. Extensive efforts are currently carry out by chemists in order to create new low bandgap materials to harvest more photons and increase the power conversion efficiency. Furthermore, processability of conjugated polymers that can be deposited from liquid solutions at low temperature make them suitable for large scale production on flexible substrates at low cost roll-to-roll process. To integrate new advanced device concepts and the nanostructure engineering of the morphology are also important in bringing high efficiency and low cost organic solar cells one step closer to successful commercialization.

5. References

- Akcelrud, L. (2003). Electroluminescent polymers. *Prog. Polym. Sci.*, Vol.28, pp.875-962.
- Alam, M.M.; Jenekhe, S.A. (2002). Polybenzobisazoles are efficient electron transport materials for improving the performance and stability of polymer light-emitting diodes. *Chem. Mater.*, Vol.14, pp.4775-4780.
- Alam, M.M.; Jenekhe, S.A. (2004). Efficient solar cells from layered nanostructures of donor and acceptor conjugated polymers. *Chem. Mater.*, Vol.16, pp.4647-4656.
- Bao, Z.; Locklin, J. (2007). *Organic Field Effect Transistors.*, Taylor & Francis, Boca Raton, FL.
- Beek, W.J.E.; Wienk, M.M.; Kemerink, M.; Yang, X.; Janssen, R.A.J. (2005). Hybrid zinc oxide conjugated polymer bulk heterojunction solar cells. *J. Phys. Chem. B*, Vol.109, pp.9505-9516.
- Bertho, S.; Oosterbaan W.D.; Vrindts, V.; DHaen, J.; Cleij, T.J.; Lutsen, L.; Manca, J.; Vanderzande, D. (2009). Controlling the morphology of nanofiber-P3HT:PCBM blends for organic bulk heterojunction solar cells. *Org. Electron.*, Vol.10, pp.1248-1251.
- Boucle', J.; Ravirajan, P.; Nelson, J. (2007). Hybrid polymer-metal oxide thin films for photovoltaic applications. *J. Mater. Chem.*, Vol.17, pp.3141-3153.
- Breeze, A.J.; Schlesinger, Z.; Carter, S.A.; Brock, P. (2001). Charge transport in TiO₂/MEH-PPV polymer photovoltaics. *J. Phys. Rev.B*, Vol.64, pp.125205-1 - 125205-9.
- Braun, D.; Heeger, A.J. (1991). Visible-light emission from semiconducting polymer diodes. *Appl. Phys. Lett.*, Vol.58, pp.1982.
- Burroughes, J.H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burns, P.L.; Holmes, A.B. (1990). Light-emitting diodes based on conjugated polymers. *Nature*, Vol.347, pp.539-541.
- Chamberlain, G.A. (1983). Organic solar cells: a review. *Solar Cells*, Vol.8, pp.47-83.
- Cheng, Y.J.; Yang, S.H.; Hsu, C.S. (2009). Synthesis of conjugated polymers for organic solar cell applications. *Chem. Rev.*, Vol.109, pp.5868-5923.
- Chiang, C.K.; Fischer, C.R.; Park, Y.W.; Heeger, A.J.; Shirakawa, H.; Louis, E.J.; Gau, S.C.; MacDiarmid, A.G. (1977). Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.*, Vol.39, pp.1098-1101.
- Chiang, C.K.; Druy, M.A.; Gau, S.C.; Heeger, A.J.; Louis, E.J.; MacDiarmid, A.G.; Park, Y.W.; Shirakawa, H. (1978). Synthesis og highly conducting films of derivatives of polyacetylene, (CH). *J. Am. Chem. Soc.*, Vol.100, pp.1013-1015.
- Colladet, K.; Fourier, S.; Cleij, T.J.; Lutsen, L.; Gelan, J.; Vanderzande, D.; Nguyen, L.H.; Neugebauer, H.; Sariciftci, S.; Aguirre, A.; Janssen, G.; Goovaerts, E. (2007). Low band gap donor-acceptor conjugated polymers toward organic solar cells applications. *Macromolecules*, Vol.40, pp.65-72.

- Dennler, G.; Sariciftci, N.S. (2005). Flexible conjugated polymer-based plastic solar cells: from basics to applications. *Proceedings of The IEEE*, Vol.93, pp.1429-1439.
- Egbe, D.A.M.; Nguyen, L.H.; Schmidtke, K.; Wild, A.; Sieber, C.; Guenes, S.; Sariciftci, N.S. (2007). Combined effects of conjugation pattern and alkoxy side chains on the photovoltaic properties of thiophene-containing PPE-PPVs. *J. Polym. Sci., Part A: Polym. Chem.*, Vol.45, pp.1619-1631.
- Egbe, D.A.M.; Nguyen, L.H.; Hoppe, H.; Mühlbacher, D.; Sariciftci, N.S. (2005). Side chain influence on electrochemical and photovoltaic properties of yne-containing poly(phenylene vinylene)s. *Macromol. Rapid Commun.*, Vol.26, pp.1389-1394.
- Forrest, S.R. (2004). The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature*, Vol.428, pp.911-918.
- Gilch, H.G.; Wheelwright, W.L. (1966). Polymerization of α -halogenated p-xylenes with base. *J. Polym. Sci., Part A: Polym. Chem.*, Vol.4, pp.1337-1349.
- Granström, M.; Petritsch, K.; Arias, A.C.; Lux, A.; Andersson, M.R.; Friend, R.H. (1998). Laminated fabrication of polymeric photovoltaic diodes. *Nature*, Vol.395, pp.257-260.
- Green, M.A.; Emery, K.; Hishikawa, Y.; Warta, W. (2010). Solar cell efficiency tables (version 35). *Prog. Photovolt. Res. Appl.*, Vol.18, pp.144-150.
- Gunes, S.; Neugebauer, H. Sariciftci, N.S. (2007). Conjugated polymer-based organic solar cells. *Chem. Rev.*, Vol.107, pp.1324-1338.
- Gupta, D.; Kabra, D.; Kolishetti, N.; Ramakrishnan, S.; Narayan, K.S. (2007). An efficient bulk-heterojunction photovoltaic cell based on energy transfer in graded-bandgap polymers. *Adv. Funct. Mater.*, Vol.17, pp.226-232.
- Hadziioannou, G.; van Hutten, P.F. (2000). *Semiconducting polymers: chemistry, physics and engineering*, 1st ed., Wiley-VCH, Weinheim, Germany.
- Hadziioannou, G.; Malliaras, G.G. (2007). *Semiconducting Polymers.*, Wiley-VCH, Weinheim, Germany.
- Halls, J.J.M.; Walsh, C.A.; Greenham, N.C.; Marseglia, E.A.; Friend, R.H.; Moratti, S.C.; Holmes, A.B. (1995). Efficient photodiodes from interpenetrating polymer networks. *Nature*, Vol.376, pp.498-500.
- Haugeneder, A.; Neges, M.; Kallinger, C.; Spirkel, W.; Lemmer, U.; Feldmann, J.; Scherf, U.; Harth, E.; Gügel, A.; Müllen, K. (1999). Exciton diffusion and dissociation in conjugated polymer/fullerene blends and heterostructures. *Phys. Rev. B.*, Vol.59, pp.15346-15351.
- Hoppe, H.; Sariciftci, N.S. (2004). Organic solar cells: an overview. *J. Mater. Res.*, Vol.19, pp.1924-1945.
- Hummelen, J.C.; Knight, B.W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C.L. (1995). Preparation and characterization of fulleroid and methanofullerene derivatives. *J. Org. Chem.*, Vol.60, pp.532-538.
- Kawano, K.; Ito, N.; Nishimori, T.; Sakai, J. (2006). Open circuit voltage of stacked bulk heterojunction organic solar cells. *Appl. Phys. Lett.*, Vol.88, pp.073514-1 - 073514-3.
- Klauk, H. (2006). *Organic Electronics.*, Wiley-VCH, Weinheim, New York.
- Shirakawa, H.; Louis, E.J.; MacMiarnid, A.G.; Chiang, C.K.; Heeger, A.J. (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$. *J. C. S. Chem. Comm.*, pp.578-580.
- Lenes, M.; Koster, L.J.A.; Mihailetschi, V.D.; Blom, P.W.M. (2006). Thickness dependence of the efficiency of polymer: fullerene bulk heterojunction solar cells. *Appl. Phys. Lett.*, Vol.88, pp.243502-1 - 243502-3.

- Li, J.; Sun, N.; Guo, Z.X.; Li, C.; Li, Y.; Dai, L.; Zhu, D.; Sun, D.; Cao, Y.; Fan, L. (2002). Photovoltaic devices with methanofullerenes as electron acceptors. *J. Phys. Chem. B*, Vol.106, pp.11509-11514.
- Mens, R.; Adriaensens, P.; Lutsen, L.; Swinnen, A.; Bertho, S.; Ruttens, B.; D'Haen, J.; Manca, J.; Cleij, T.; Vanderzande, D.; Gelan, J. (2008). NMR study of the nanomorphology in thin films of polymer blends used in organic PV devices: MDMO-PPV/PCBM. *J. Polym. Sci., Part A: Polym. Chem.*, Vol.46, pp.138-145.
- Moliton, A. (2006). *Optoelectronics of Molecules and Polymers.*, Springer-Verlag, Berlin, Germany.
- Mozer, A.; Sariciftci, N.S. (2006). Conjugated polymer photovoltaic devices and materials. *Chimie*, Vol.9, pp.568-577.
- Nalwa, H.S. (2008). *Handbook of Organic Electronics and Photonics.*, American Scientific Publishers, Valencia, CA.
- Neef, C.J.; Ferraris, J.P. (2000). MEH-PPV: Improved synthetic procedure and molecular weight control. *Macromolecules*, Vol.33, pp.2311-2314.
- Neyshtadt, S.; Kalina, M.; Frey, G.L. (2008). Self-organized semiconducting polymer-incorporated mesostructured titania for photovoltaic applications. *Adv. Mater.*, Vol.20, pp.2541-2546.
- Onsager, L. (1938). Initial recombination of ions. *Phys. Rev.*, Vol.54, pp.554-557.
- Pacios, R.; Chatten, A.J.; Kawano, K.; Durrant, J.R.; Bradley, D.D.C.; Nelson, J. (2006). Effects of photo-oxidation on the performance of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]:[6,6]-phenyl C-61-butyric acid methyl ester solar cells. *Adv. Funct. Mater.*, Vol.16, pp.2117-2126.
- Padinger, F.; Rittberger, R.S.; Sariciftci, N.S. (2003). Effects of postproduction treatment on plastic solar cells. *Adv. Funct. Mater.*, Vol.13, pp.85-88.
- Park, J.; Han, S.H.; Senthilarasu, S.; Lee, S.H. (2007). Improvement of device performances by thin interlayer in conjugated polymers/methanofullerene plastic solar cell. *Sol. Energy Mater. Sol. Cells*, Vol.91, pp.751-753.
- Park, S.H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J.S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A.J. (2009). Bulk heterojunction solar cells with internal quantum efficiency approaching 100%. *Nat. Photon.*, Vol.3, pp.297-303.
- Parker, I.D. (1994). Carrier tunneling and device characteristics in polymer light-emitting diodes. *J. Appl. Phys.*, Vol.75, pp.1656-1666.
- Papadimitrakopoulos, F.; Konstadinidis, K.; Miller, T.M.; Opila, R.; Chandross, E.A.; Galvin, M.E. (1994). The Role of Carbonyl Groups in the Photoluminescence of Poly(*p*-phenylenevinylene). *Chem. Mater.*, Vol.6, pp.1563-1568.
- Peet, J.; Kim, J.Y.; Coates, N.E.; Ma, W.L.; Moses, D.; Heeger, A.J.; Bazan, G.C. (2007). Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols. *Nat. Mater.*, Vol.6, pp.497-500.
- Sariciftci, N.S.; Smilowitz, L.; Heeger, A.J.; Wudl, F. (1992). Photoinduced electron-transfer from a conducting polymer to buckminsterfullerenes. *Science*, Vol.258, pp.1474-1476.
- Shaheen, S.E.; Brabec, C.J.; Sariciftci, N.S.; Padinger, F.; Fromherz, T.; Huneelen, J.C. (2001). 2.5% efficient organic plastic solar cells. *Appl. Phys. Lett.*, Vol.78, pp.841-843.
- Shim, H.S.; Na, S.I.; Nam, S.H.; Ahn, H.J.; Kim, H.J.; Kim, D.Y.; Kim, W.B. (2008). Efficient photovoltaic device fashioned of highly aligned multilayers of electrospun TiO₂ nanowire array with conjugated polymer. *Appl. Phys. Lett.*, Vol.92, pp.183107-1 - 183107-3.

- Shinar, R.; Shinar, J. (2009). *Organic Electronics in Sensors and Biotechnology.*, McGraw-Hill, New York.
- Shirakawa, H. (2001). Die Entdeckung der Polyacetylenefilme – der Beginn des Zeitalters leitfähiger Polymere (Nobel – Aufsatz). *Angew. Chem.*, Vol.113, pp.2642-2628.
- Shrotriya, V.; Wu, E.H.E.; Li, G.; Yao, Y.; Yang, Y. (2006). Efficient light harvesting in multiple-device stacked structure for polymer solar cells. *Appl. Phys. Lett.*, Vol.88, pp.064104-1 – 064104-3.
- Song, M.Y.; Kim, K.J.; Kim, D.Y. (2005). Enhancement of photovoltaic characteristics using a PEDOT interlayer in TiO₂/MEHPPV heterojunction devices. *Sol. Energy Mater. Sol. Cells*, Vol.85, pp.31-39.
- Skotheim, T.J.; Elsenbaumer, R.L.; Reynolds, J.R. (1998). *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York.
- Sun, B.; Marx, E.; Greenham, N.C. (2003). Photovoltaic devices using blends of branched CdSe nanoparticles and conjugated polymers. *Nano Lett.*, Vol.3, pp.961-963.
- Sun, S.S.; Dalton, L. (2008). *Introduction to Organic Electronic and Optoelectronic Materials and Devices.*, Taylor & Francis, Boca Raton, FL.
- Tajima, K.; Suzuki, Y.; Hashimoto, K. (2008). Polymer photovoltaic devices using fully regioregular poly[(2-methoxy-5-(3',7'-dimethyloctyloxy))-1,4-phenylenevinylene]. *J. Phys. Chem. C*, Vol.112, pp.8507-8510.
- Tang, C.W. (1986). 2-Layer Organic Photovoltaic Cell. *Appl. Phys. Lett.*, Vol.48, pp.183-185.
- Thompson, B.C.; Kim, Y.G.; Reynolds, J.R. (2005). Spectral broadening in MEH-PPV : PCBM-based photovoltaic devices via blending with a narrow band gap cyanovinylene-dioxythiophene polymer. *Macromolecules*, Vol.38, pp.5359-5362.
- Thompson, B.C.; Kim, Y.G.; McCarley, T.D.; Reynolds, J.R. (2006). Soluble narrow band gap and blue propylenedioxythiophene-cyanovinylene polymers as multifunctional materials for photovoltaic and electrochromic applications. *J. Am. Chem. Soc.*, Vol.128, pp.12714-12725.
- van Hal, P.A.; Wienk, M.M.; Kroon, J.M.; Verhees, W.J.H.; Slooff, L.H.; van Gennip, W.J.H.; Jonkheijm, P.; Janssen, R.A.J. (2003). Photoinduced electron transfer and photovoltaic response of a MDMO-PPV:TiO₂ bulk-heterojunction. *Adv. Mater.*, Vol.15, pp.118-121.
- Wei, Q.; Hirota, K.; Tajima, K.; Hashimoto, K. (2006). Design and Synthesis of TiO₂ Nanorod Assemblies and Their Application for Photovoltaic Devices. *Chem. Mater.*, Vol.18, pp.5080-5087.
- Wessling, R.A.; Zimmerman, R.G. (1968). U.S. Patent 3401152.
- Wessling, R.A. (1985). The polymerization of xylylene bisdialkyl sulfonium salts. *J. Polym. Sci., Polym. Symp.*, Vol.72, pp.55-66.
- Wohrle, D.; Meissner, D. (1991). Organic Solar Cells. *Adv. Mater.*, Vol.3, pp.129-138.
- Yu, G.; Gao, J.; Hummelen, J.C.; Wudl, F.; Heeger, A.J. (1995). Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunction. *Science*, Vol.270, pp.1789-1791.
- Yu, G.; Wang, J.; McElvain, J.; Heeger, A.J. (1998). Large-area, full-color image sensors made with semiconducting polymers. *Adv. Mater.*, Vol.10, pp.1431-1434.
- Zhang, F.L.; Johansson, M.; Andersson, M.R.; Hummelen, J.C.; Inganäs, O. (2002). Polymer photovoltaic cells with conducting polymer anodes. *Adv. Mater.*, Vol.14, pp.662-665.